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MERCURY OCCURRENCE IN SEDIMENT CORES FROM WESTERN LAKE ERIE[1]

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ABSTRACT

The Detroit River is the major source of mercury contamination in the sediments of western Lake Erie. Analyses of 63 sediment cores indicate that the mercury consists of two components: a high-concentration (0.5 to 4.0 ppm of dry sediment) mercury-enriched surface zone, whose concentration decreases pseudo-exponentially with depth, and a low-concentration (0.04 to 0.09 ppm of dry sediment) relatively constant-background zone. Mathematical modeling of the mercury concentration as a function of depth in these sediment cores and subsequent statistical analysis of the apparent constant-concentration levels reveals that two log-normal distributions are necessary to describe these observed constant concentrations. Any mercury concentration within the sediment in excess of the lower (natural) background level plus one standard deviation is defined as being due to pollution. Such calculations of the pollution component for these 63 cores serve as the basis for an estimate of the total mercury that has been added through pollution sources. The mercury-pollution load for bottom sediments of western Lake Erie is estimated to be 228 metric tons.

INTRODUCTION

Discovery of mercury contamination in the St. Clair River-Lake St. Clair-Detroit River-Lake Erie system generated great public interest in the mercury levels of water and fish in this system (Seagram, 1970). Subsequent banning of sport and commercial fishing led to testing for trace mercury by various state and federal agencies (Kalb, 1970). The Federal Water Quality Administration (1970) conducted a survey of fish, water, and sediment to define the extent of the pollution and to determine its major sources. A similar survey was made and a report was prepared by the Ontario Water Resources Commission (1970) for Canadian waters.

Two chemical plants, Dow Chemical Corporation, Sarnia, Ontario, and BASF Wyandotte Chemical Corporation, Wyandotte, Michigan, were identified as major contributors to the mercury pollution of Lake Erie, both by these government reports and independently by Copeland (1970). These companies manufacture chlorine gas and caustic soda by the electrolytic process, which involves the electrolysis of brine to produce chlorine gas and a mercury-sodium metal amalgam. The amalgam is contacted with water to produce sodium hydroxide, the mercury metal being recycled to the electrolytic cell. The rate of accidental mercury release from these two plants has been estimated to be 22.7 kg per day from 1950 to 1970 for the Dow Chemical plant and 4.5 to 9.1 kg per day from 1939 to 1970 for the BASF Wyandotte plant (Federal Water Quality Administration, 1970).

Previous studies of mercury concentration in the Great Lakes point out the importance of industrial-mercury input. Thomas (1972) concludes that the con-

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centration of mercury in recent sediments of Lake Ontario could be accounted for by assuming an average minimum daily input of 56.7 kg of mercury, of which he estimates that 37.6 kg came from industrial sources and the remaining 19.0 kg from natural sources. Using pollen analyses to establish dates, Thomas (1972) suggests that industrial mercury input began about 1900, rose rapidly up until 1943, and then rose more slowly to 1970. The work of Kennedy *et al.* (1971) shows that mercury in sediments in southern Lake Michigan is concentrated at the top of the sediment core, with decreasing concentrations with increasing depth. The total mercury content of Lake Michigan sediments decreases rapidly from 0.1 to 0.4 ppm at the sediment surface to about 0.05 ppm at 10 cm below the sediment-water interface.

A major objective of our study was to establish the natural background level for mercury in western Lake Erie sediments and to estimate pollution loading. Mercury pollution is defined as any significant load of this metal above the background value. The standard deviation of the natural background mercury level was used as the measure of significance. In this respect, mercury pollution is defined as a mercury level in excess of one standard deviation above the natural background level. After the background value and its standard deviation were established, the total pollution contribution was calculated, based on a mathematical model of the mercury concentration in the sediments as a function of depth within the sediment cores.

METHODS

A joint limnological survey organized by The Ohio State University Center for Lake Erie Area Research, using the 46-foot research boat *GS–1* supplied by the Ohio Division of Geological Survey, was conducted July 19–29, 1971, to sample water, sediments, and benthic organisms and to make physicochemical measurements. Participants were from Bowling Green State University, John Carroll University, The Ohio State University (CLEAR), and the Ohio Division of Geological Survey. The sediment cores were obtained by a hand-driven coring device consisting of an aluminum pipe shaft, poppit check valve, core barrel, and 1½-inch- (3.8-cm-) diameter cellulose-acetate-butyrate core liner. Sediment cores were obtained from 63 of the 69 stations shown in figure 1. These stations were established on a 5-minute latitude-longitude grid pattern in western Lake Erie, with extra stations for additional detail located at the mouths of the Detroit and Maumee Rivers.

The sediment cores, which ranged in length from 5 to 60 cm, were divided into 1- to 2-cm sections. Four or five of these sections from each core were digested in a concentrated sulfuric-nitric acid mixture (following the methods of Skoch and Turk, 1972) and then analyzed for mercury, using the flameless atomic absorption procedure of Hatch and Ott (1968). To avoid any loss of mercury from the sediment due to drying, the samples used for mercury analysis were not dried prior to weighing. A second portion of the sediment was dried at 110°C and used to calculate the water content. Based on the water content, the mercury analyses presented in this paper are corrected to a dry-sediment basis.

RESULTS AND DISCUSSION

The results of the mercury analyses of the sediment core intervals are contained in table 1. Each of these values represents a single analysis. The results of a few duplicate analyses indicated that the error associated with these determinations is ±15 percent of the stated value. Results of the water analyses obtained at the sampling stations in this study are contained in a report by Kovacik (1972a).

A mathematical model can be used to describe the mercury concentration in the sediment cores as a function of depth. This model consists of a two-term

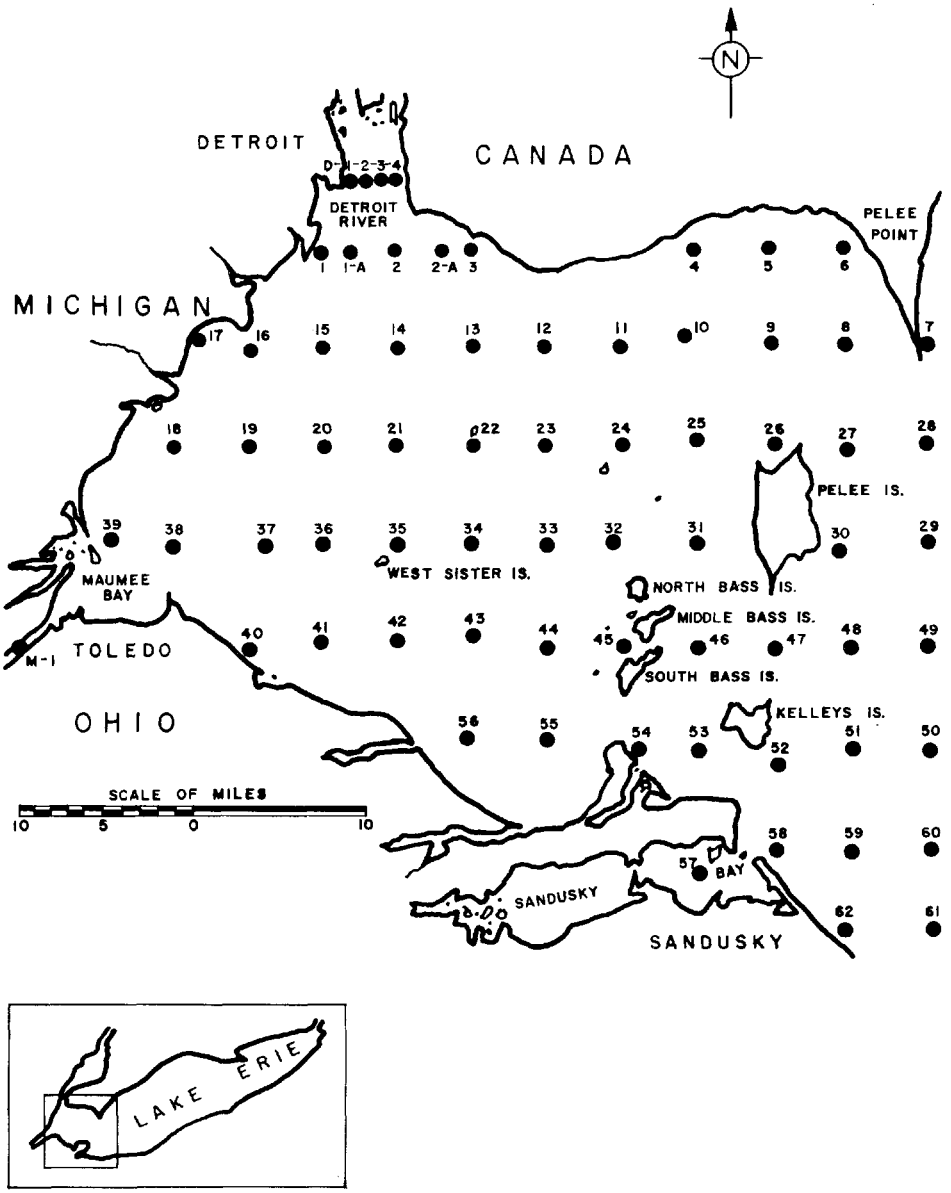

FIGURE 1. Sampling stations in western Lake Erie.

equation having a rapidly decreasing exponential term and a constant, as follows:

$$Hg(D) = Ae^{-\lambda D} + C \qquad \text{(Equation 1)}$$

where Hg (D) = the total mercury concentration in the sediment at depth D below the sediment-water interface,
A = the surface intercept of the rapidly decreasing term,
λ = the decay constant,
D = the depth below the sediment water interface, and
C = a constant which represents the sum of the background mercury concentration and other apparently constant mercury inputs.

TABLE 1

Mercury concentrations and water content of sediments from the western basin of Lake Erie

Station no.	Depth (cm)	Water (wt. %)	Mercury (ppm dry basis)
1	0–1	57	3.8
	3–4	51	5.8
	9–10	48	4.9
	15–16	42	2.8
	25–26.5	30	0.60
1A	0–2	42	0.97
	5–6	44	0.86
	10–11	45	0.98
	19–20	46	1.6
	35–36.5	48	0.68
2	0–1	52	2.3
	1–2	50	3.4
	3–4	42	2.9
	5–6	33	2.1
	8.5–9.5	40	2.1
2A	0–1	28	0.52
	1–2	20	0.30
	2–3	20	0.17
	3–4	22	0.35
	5–6.5	24	0.32
3	0–1	24	0.24
	1–2	23	0.24
	3–4	17	0.28
	5–6	20	0.21
	8–9	25	0.58
4	0–2	52	1.6
	5–6	48	1.1
	10–11	42	0.72
	19–20	30	0.090
	39–40	24	0.054
	57–58	22	0.048
5	0–2	57	1.3
	5–6	56	1.4
	10–11	42	1.0
	19–20	32	0.081
	39–40	26	0.038
	56–57	22	0.046
6	0–2	46	1.0
	5–6	34	0.68
	9–10	32	0.33
	15–16	20	0.065
	32–33.6	26	0.037
7	0–1	22	0.13
	1–2	18	0.16
8	0–2	44	0.48
	5–6	34	0.12
	15–16	29	0.082
	22.5–23.5	30	0.044
	45–46	30	0.044
9	0–2	59	1.3
	5–6	55	0.86
	10–11	56	0.75
	19–20	41	0.068
	42–43.7	32	0.12
10	0–2	56	1.6
	2–4	58	1.8
	9–10	50	1.1
	22–23	34	0.17
	48–49.5	36	0.34

TABLE 1. *Continued*

Station no.	Depth (cm)	Water (wt. %)	Mercury (ppm dry basis)
11	0–2	41	0.052
	5–6	39	0.073
	15–16	33	0.052
	26–27.2	31	0.058
	55–56.5	32	0.037
12	0–2	36	0.088
	5–6	38	0.089
	10–11	35	0.069
	19–20	28	0.14
	59–60	32	0.079
13	0–2	42	1.8
	5–6	31	0.12
	9–10	28	0.044
	15–16	28	0.067
	19–20	29	0.044
	39–40	26	0.044
	57–58	26	0.033
14	0–2	50	2.0
	2–4	36	0.86
	4–6	23	0.16
	6–8	64	0.56
	8–10	23	0.21
	10–12	17	0.12
	12–14	22	0.18
	14–16	20	0.12
	16–19	21	0.13
15	0–1	58	4.0
	1–2	53	3.0
	6–7	70	4.5
	9.8–10.8	36	0.81
16	0–1	59	2.9
	3–4	54	3.6
	9–10	43	1.1
	15–16	32	0.52
	27–28.4	34	0.25
18	0–1	54	1.3
	1–2	26	0.60
	2–3	43	0.64
	3–4	33	0.34
	7–8	28	0.053
19	0–1	44	1.2
	1–2	34	0.70
	3–4	24	0.18
	5–6	24	0.11
	8.8–9.8	28	0.066
20	0–1	36	0.50
	1–2	32	0.50
	2–3	23	0.14
	3–4.5	21	0.14
21	0–1	42	0.34
	3–4	28	0.21
	9–10	36	0.20
	28–29	38	0.12
	60–61.4	33	0.22
22	0–2	46	0.43
	5–6	42	0.42
	9–10	44	0.38
	15–16	42	0.20
	19–20	37	0.10
	59–60	32	0.055
23	0–2	62	0.12
	5–6	41	0.065

TABLE 1. *Continued*

Station no.	Depth (cm)	Water (wt. %)	Mercury (ppm dry basis)
	9–10	38	0.069
	15–16	36	0.052
	19–20	42	0.048
	39–40	30	0.049
	58–59	32	0.053
24	0–2	26	0.056
	5–6	28	0.068
	15–16	27	0.076
	27–28	24	0.034
	57–58.5	34	0.047
25	0–2	58	1.1
	5–6	50	0.66
	10–11	40	0.16
	19–20	40	0.082
	54–55	40	0.094
26	0–1	29	0.30
	3–4	22	0.16
	9–10	18	0.16
	15–16	20	0.18
	20–21.3	18	0.14
28	0–1	48	0.26
	1–2	41	0.20
	2–3	26	0.089
29	0–1	56	0.45
	1–2	27	0.16
	5–6	24	0.18
	9–10	23	0.48
	22–23	21	0.26
31	0–1	26	0.14
	1–2	44	0.12
	2–3	37	0.080
	3–4	40	0.082
	4–5.5	39	0.052
32	0–2	50	0.067
	5–6	36	0.072
	9–10	34	0.079
	15–16	35	0.078
	19–20	34	0.050
	39–40	32	0.047
	54–55	40	0.080
33	0–2	62	1.7
	5–6	50	0.67
	10–11	50	0.16
	19–20	44	0.099
	39–40	40	0.091
	56–57	34	0.062
34	0–2	58	1.8
	5–6	54	0.38
	17–18.5	47	0.065
	29–30	37	0.040
	37–38.5	39	0.028
35	0–2	58	1.8
	5–6	52	0.92
	10–11	46	0.48
	19–20	44	0.26
	52–53	38	0.052
36	0–1	48	1.0
	1–2	37	0.56
	5–6	20	0.28
	9–10	20	0.15
	12–13	34	0.14

TABLE 1. *Continued*

Station no.	Depth (cm)	Water (wt. %)	Mercury (ppm dry basis)
37	0–2	33	1.4
	5–6	32	0.44
	15–16	36	0.25
	28–29	31	0.10
	52–53	34	0.072
38	0–2	42	0.20
	5–6	31	0.15
	10–11	36	0.24
	15–16	34	0.23
	29–30.7	21	0.036
39	0–1	36	0.32
	1–2	35	0.28
	5–6	26	0.22
	9–10	24	0.21
	17–18.5	23	0.16
40	0–1	29	0.035
	1–2	28	0.028
	2–3	24	0.022
	3–4	24	0.0057
	6–7.5	32	0.028
43	0–2	62	1.8
	5–6	50	0.50
	10–11	52	0.32
	15–16	40	0.14
	30–31.5	36	0.032
44	0–2	62	1.0
	5–6	52	0.42
	10–11	50	0.34
	19–20	38	0.12
	37–38	40	0.088
45	0–2	34	0.080
	5–6	30	0.053
	9–10	32	0.075
	15–16	26	0.062
	19–20	28	0.070
	57–58	66	0.20
46	0–1	49	0.43
	3–4	27	0.22
	9–10	28	0.26
	20–21	30	0.10
	47–48.8	42	0.16
47	0–2	62	0.52
	5–6	40	0.32
	15–16	23	0.020
	25–26	26	0.010
	46–47.6	20	0.0052
48	0–2	36	0.16
	5–6	29	0.083
	9–10	31	0.055
	15–16	28	0.032
	19–20	28	0.039
	59–60	26	0.036
49	0–2	41	0.020
	5–6	28	0.047
	10–11	30	0.023
	19–20	30	0.058
	59–60.4	31	0.041
50	0–1	52	0.44
	1–2	44	0.32
	5–6	41	0.23
	9–10	36	0.17
	20–21	32	0.16

TABLE 1. *Continued*

Station no.	Depth (cm)	Water (wt. %)	Mercury (ppm dry basis)
51	0–2	38	0.054
	5–6	38	0.050
	10–11	30	0.068
	19–20	27	0.042
	39–40	25	0.045
	59–60	33	0.072
52	0–2	47	0.60
	5–6	42	0.51
	9–10	36	0.16
	15–16	32	0.26
	19–20	30	0.051
	60–61	22	0.044
53	0–1	34	0.34
	1–2	27	0.23
	5–6	20	0.14
	9–10	18	0.12
	12–13	24	0.12
55	0–2	60	0.79
	5–6	48	0.52
	15–16	21	0.15
	23.5–25	28	0.076
	50–51.3	60	0.073
56	0–1	45	0.75
	3–4	42	0.54
	9–10	28	0.14
	15–16	34	0.39
	26–27.5	22	0.20
57	0–2	52	0.34
	5–6	53	0.44
	10–11	47	0.39
	19–20	47	0.31
	34–35	39	0.12
58	0–1	48	0.076
	1–2	20	0.019
	2–3	18	0.020
	3–4	19	0.024
	6–7.3	26	0.068
59	0–2	46	0.29
	5–6	36	0.068
	10–11	34	0.048
	19–20	33	0.044
	39–40	28	0.046
	59–60	32	0.053
60	0–2	65	0.67
	5–6	56	0.24
	10–11	40	0.088
	19–20	37	0.13
	32–33	30	0.032
61	0–2	64	0.56
	5–6	60	0.56
	10–11	56	0.48
	19–20	44	0.20
	53–54.5	36	0.084
62	0–1	38	0.20
	1–2	42	0.26
	5–6	34	0.24
	11–12	43	0.16
	18–19.2	22	0.056
D–1	0–1	34	1.9
	1–2	34	2.0
	5–6	20	1.2
	9–10	26	1.3
	16–17.6	24	0.74

TABLE 1. *Continued*

Station no.	Depth (cm)	Water (wt. %)	Mercury (ppm dry basis)
D-2	0–1	37	0.96
	1–2	28	0.72
	8–9	32	0.66
	12–13	21	0.30
	17–18	18	0.13
D-3	0–1	35	0.0075
	1–2	26	0.0055
	2–3	26	0.0069
	3–4	24	0.0026
	6–7	26	0.0056
D-4	0–1	48	2.0
	1–2	34	0.82
	2–3	26	0.66
	3–4	21	0.54
M-1	0–2	50	0.65
	5–6	42	0.72
	19–20	38	1.4
	29–30	40	0.50
	56–57.5	36	0.86

The parameters representing the least-squares fit of the mathematical model (Equation 1) for the sediment cores are given in table 2. The least-squares calculations were done using the computer program FRANTIC (Rogers, 1962).

The mathematical form of Equation 1 is similar to the integrated form of equations that describe radioactive decay, except that radioactive-decay equations are a function of time instead of depth. A useful concept in working with

TABLE 2

Mathematical models of mercury concentration and porosity in Lake Erie sediments

Station	Mercury-depth model			Porosity-depth model			Polluted depth (cm)
	A (ppm Hg)	λ (cm^{-1})	C (ppm Hg)	A (vol. frac.)	λ (cm^{-1})	C (vol. frac.)	
1	5.4	0.0667	0.	0.54	0.0231	0.25	20.0
1-A	0.		0.98	0.41	−0.0028	0.25	20.0
2	3.7	0.0748	0.	0.19	0.429	0.25	20.0
2-A	0.		0.32	0.19	0.0056	0.25	20.0
3	0.		0.31	0.		0.42	20.0
4	1.9	0.136	0.054	0.38	0.0422	0.39	20.0
5	1.6	0.117	0.019	0.41	0.0463	0.40	20.0
6	1.2	0.167	0.023	0.29	0.183	0.46	20.0
8	0.63	0.398	0.051	0.18	0.278	0.53	9.3
9	1.5	0.145	0.064	0.53	0.0154	0.28	20.0
10	1.8	0.121	0.21	0.24	0.0724	0.57	20.0
11	0.		0.055	0.11	0.0901	0.54	0.0
12	0.		0.092	0.33	0.0026	0.25	20.0
13	3.4	0.690	0.044	0.21	0.269	0.49	7.2
14	2.9	0.471	0.13	0.47	0.394	0.41	20.0
15	3.7	0.155	0.	0.55	0.0426	0.25	20.0
16	3.5	0.122	0.10	0.28	0.107	0.54	20.0
18	1.5	0.431	0.	0.52	0.106	0.25	7.2
19	1.7	0.723	0.066	0.35	0.632	0.42	11.2
20	0.68	0.476	0.	0.39	0.247	0.25	4.9
21	0.21	0.453	0.18	0.09	0.203	0.58	20.0

TABLE 2. *Continued*

Station	Mercury-depth model			Porosity-depth model			Polluted depth (cm)
	A (ppm Hg)	λ (cm^{-1})	C (ppm Hg)	A (vol. frac.)	λ (cm^{-1})	C (vol. frac.)	
22	0.46	0.0721	0.042	0.19	0.0263	0.50	20.0
23	0.089	0.271	0.051	0.30	0.169	0.55	6.4
24	0.		0.056	0.25	0.0049	0.25	0.0
25	1.3	0.206	0.071	0.18	0.174	0.63	20.0
26	0.23	0.937	0.16	0.17	0.282	0.37	20.0
28	0.36	0.508	0.	0.55	0.307	0.25	3.3
29	0.		0.31	0.71	1.79	0.44	20.0
31	0.17	0.238	0.	0.41	0.0226	0.25	4.0
32	0.013	0.0522	0.059	0.23	0.548	0.58	8.5
33	2.2	0.269	0.073	0.22	0.0503	0.58	20.0
34	2.4	0.353	0.038	0.26	0.0293	0.53	12.5
35	2.0	0.138	0.059	0.18	0.0655	0.61	20.0
36	1.0	0.496	0.16	0.42	0.434	0.38	20.0
37	1.6	0.259	0.10	0.		0.56	20.0
38	0.23	0.0488	0.	0.43	0.0283	0.25	20.0
39	0.18	0.128	0.14	0.20	0.248	0.44	20.0
40	3.7	0.310	0.	0.29	0.0977	0.25	13.0
43	2.1	0.226	0.037	0.28	0.0542	0.54	18.8
44	1.1	0.181	0.090	0.22	0.0944	0.61	20.0
45	0.		0.068	0.10	0.104	0.49	20.0
46	0.30	0.224	0.14	0.29	0.630	0.51	20.0
47	0.67	0.210	0.003	0.45	0.143	0.42	11.2
48	0.17	0.232	0.034	0.11	0.146	0.49	7.1
49	0.		0.038	0.21	0.669	0.53	0.0
50	0.30	0.305	0.159	0.19	0.116	0.57	20.0
51	0.		0.056	0.18	0.0616	0.45	0.0
52	0.70	0.155	0.033	0.30	0.0504	0.42	19.6
53	0.29	0.670	0.13	0.25	0.507	0.38	20.0
55	0.86	0.138	0.060	0.56	0.0465	0.25	20.0
56	0.70	0.325	0.197	0.46	0.0322	0.25	20.0
57	0.39	0.0278	0.	0.50	0.0076	0.25	20.0
58	0.		0.038	0.		0.47	0.0
59	0.41	0.55	0.048	0.18	0.170	0.54	5.6
60	0.80	0.26	0.048	0.35	0.0739	0.51	14.4
61	0.59	0.0517	0.045	0.30	0.0364	0.55	20.0
62	0.27	0.0676	0.	0.40	0.0421	0.25	20.0
D-1	2.0	0.0584	0.	0.20	0.711	0.45	20.0
D-2	0.96	0.095	0.	0.28	0.0265	0.25	20.0
D-3	0.066	0.105	0.	0.25	1.93	0.47	0.0
D-4	2.2	0.487	0.	0.54	0.334	0.25	7.2
M-1	0.		0.69	0.13	0.186	0.61	20.0

radioactivity is the term "half-life," which is defined as the time required for the activity to decrease by one-half or

$$t_{1/2} = ln2/\lambda \qquad \text{(Equation 2)}$$

where $t_{1/2}$ = the half-life,
$ln2$ = the natural logarithm of 2 (0.693), and
λ = the decay constant.

By analogy it is very useful to define a term called "half-depth," the distance (depth) in cm required for the mercury concentration in the sediment core to be reduced by one-half, and expressed as

$$D_{1/2} = ln2/\lambda \qquad \text{(Equation 3)}$$

where $D_{1/2}$ = the half-depth,
$ln2$ = the natural logarithm of 2 (0.693), and
λ = the decay constant.

Two processes interact to produce the mercury concentration-depth relationship (Equation 1) reflected by the half-depth values shown in figure 2. First, mercury from pollution sources and mercury from mineral material are added to the lake bottom somewhat independently, but mineral material makes up most of the bulk of the sediment. The mercury, regardless of chemical form, is added to the sediments via organic detritus (Cline *et al.*, 1973) and decaying biomass, and is associated with organic coatings on sediment particles (Cranston and

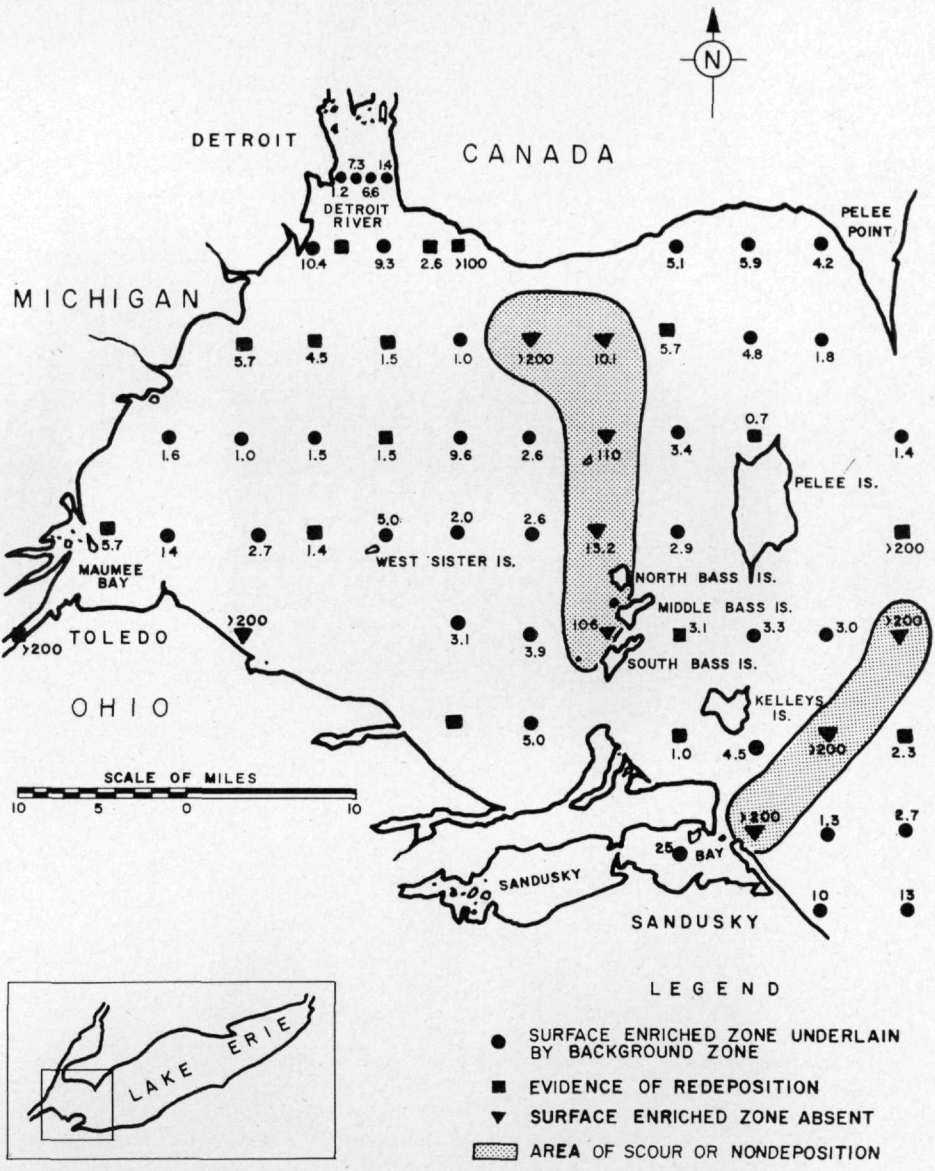

FIGURE 2. Half-depth values for mercury in sediment cores from western Lake Erie. Station symbols indicate the pattern of mercury concentration within the sediment core as follows: circle — mercury-enriched surface zone underlain by zone having background mercury levels, square — evidence of redeposited sediments, and triangle — mercury-enriched surface zone absent.

Buckley, 1972). Since the organic fraction of the sediment makes up only about 1–5 percent and the mass of mercury is insignificant, the effect of an increase in the pollution-mercury flux to the sediment column is the same as a decrease in the flux of mineral material to the sediments.

The second process that affects the half-depth values is scouring by currents, leading to resuspension and redeposition of polluted surface sediments, and resulting in a homogenization of the sediment and its included mercury concentration. Half-depth values in excess of 50 cm may result from this process. Nondeposition or very low rates of deposition result in ambiguous values of half-depth, because the controlling parameters are the ratio of organic-to-mineral input and the sedimentation rate. Moderately high values of mercury half-depth were observed in the areas of high rates of sedimentation: at the mouth of the Detroit River, in Maumee Bay, in Sandusky Bay and immediate area, and in the deep central part of the western basin.

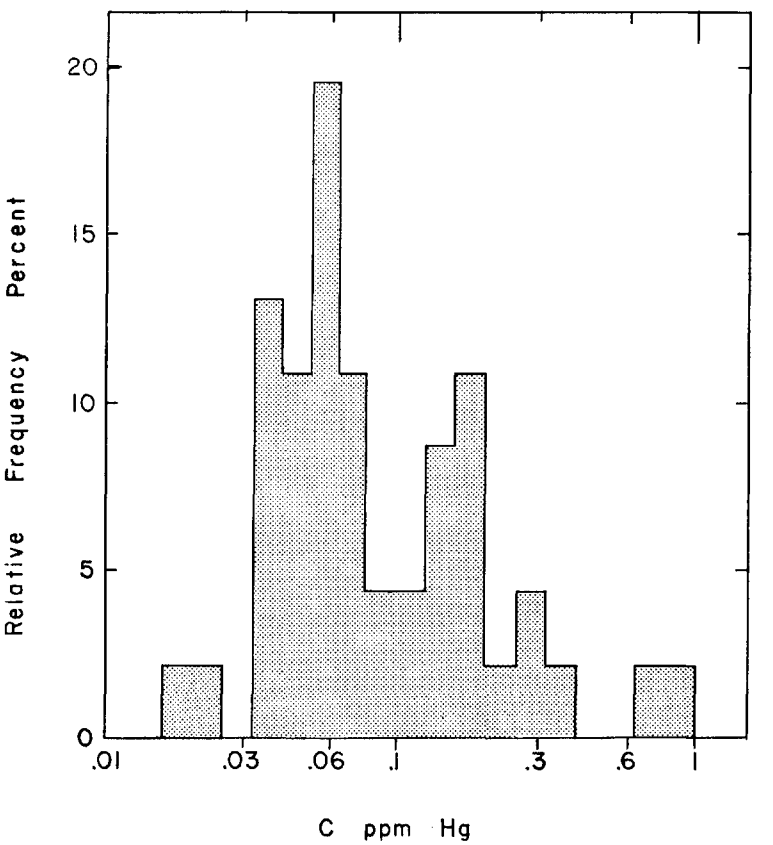

FIGURE 3. Frequency histogram of parameter C from mercury-depth models in table 2.

The frequency histogram (fig. 3) of the non-zero values of the parameter C (Equation 1) for the mercury-depth model from table 2 indicates that the values are lognormal and bimodally distributed. Computer analysis of the data in figure 3, using the program MAXLIKE by Jones and James (1972), gives the first mode as $10^{-1.32 \pm 0.10}$, or 0.048 ppm, and the second mode as $10^{-0.95 \pm 0.39}$, or 0.11 ppm.

Resuspension and redeposition of polluted surface sediments can produce a relatively constant concentration of mercury as a function of depth; this concentration is greater than the natural background level of 0.02 to 0.07 ppm dry basis.

The lower mode in figure 3 represents the natural background amount of mercury associated with the source rocks from which the sediment has been derived and is in agreement with Cameron and Jonasson (1972), Syers *et al.* (1973), and Kennedy *et al.* (1971). Cameron and Jonasson (1972) obtained a median mercury concentration of 0.08 ppm for the Precambrian shales of the Canadian shield area to the north of the Great Lakes. The glacial till which covers much of the surface in the western Lake Erie drainage basin is derived in part from these Precambrian rocks to the north and thus should have a similar mercury concentration. Kennedy *et al.* (1971) observed a similar value, 0.03 to 0.06 ppm, for the background level of mercury in the sediments on the bottom of southern Lake Michigan. The water in southern Lake Michigan is very much deeper than is that of western Lake Erie. Therefore these Lake Michigan sediments should not have been appreciably affected by any processes of resuspension and redeposition.

The second mode, at 0.11 ppm mercury, is considered to be a product of the work of the resuspension-redeposition process in western Lake Erie. Many of the cores represented by this higher mode are located in areas of concentrated ship traffic, as shown by the squares in figure 2. The prop wash from a large ship can be very effective in stirring up the bottom sediments. Many of these same cores are also located in areas subject to scour from natural bottom currents at the mouth of the Detroit River.

Four patterns of mercury concentration-depth relationships are contained in the data in table 1. Examples of these patterns are shown in figures 4a, b, c, and d. The typical pattern of the variation in mercury concentration with depth shown in figure 4a for Station 4 contains a mercury-enriched surface zone overlying a zone having a natural background level of mercury. The mercury concentration within the surface zone decreases pseudo-exponentially with depth. This exponential decrease may be due either to an exponential increase in the mercury input to the sediments within the last 30–40 years or to the establishment of a reaction-diffusion controlled gradient as a result of movement of mercury within the upper 10–30 cm of sediment. The reaction-diffusion models of Anikouchine (1967), and Manheim (1970), and Tazur (1971) all predict an exponential decrease in metal concentration with depth below the sediment-water interface. These reaction-diffusion models are consistent with reactions having first-order kinetics. Two possible reactions are the methylation of metallic mercury by microorganisms to form mono-methyl mercury (CH_3Hg^+), as described by Wood (1968), or the alteration of the organic component in the sediment with diagenesis resulting both in a loss of binding sites for inorganic mercury (Hg^+ or Hg^{2+}) and in subsequent migration of the mercury ions upward toward a zone containing organic material with adequate binding sites.

The second pattern of mercury concentration with depth is shown by Station 11 in figure 4b. The mercury level is essentially constant at all depths and has a value within the first or natural background mode in figure 3. This type of pattern represents either the combination of scouring of the sediment surface and removal of the mercury-enriched surface zone, or nondeposition during the past 10 to 40 years, or some combination of these processes.

In about 25 percent of the cores, the effects of resuspension-homogenization-redeposition were shown by the presence of abnormally high levels of mercury (greater than 0.08 ppm) that did not vary appreciably over the interval of the core. These abnormal levels may have been below a mercury-enriched surface zone, as for Station 14 (fig. 4c), or may have extended all the way up to the sediment surface, as in Station 1–A (fig. 4d). The criterion for abnormality that was

used was whether the value of C, in the mercury-depth model (Equation 1), was greater than 0.0675 ppm mercury dry basis, the mean-plus-one standard deviation ($1.0^{-1.32+0.10}$) of the lower mode in figure 3, as determined by the program MAX-LIKE (Jones and James, 1972). This critical level of mercury concentration is shown in figure 4 by a dashed line.

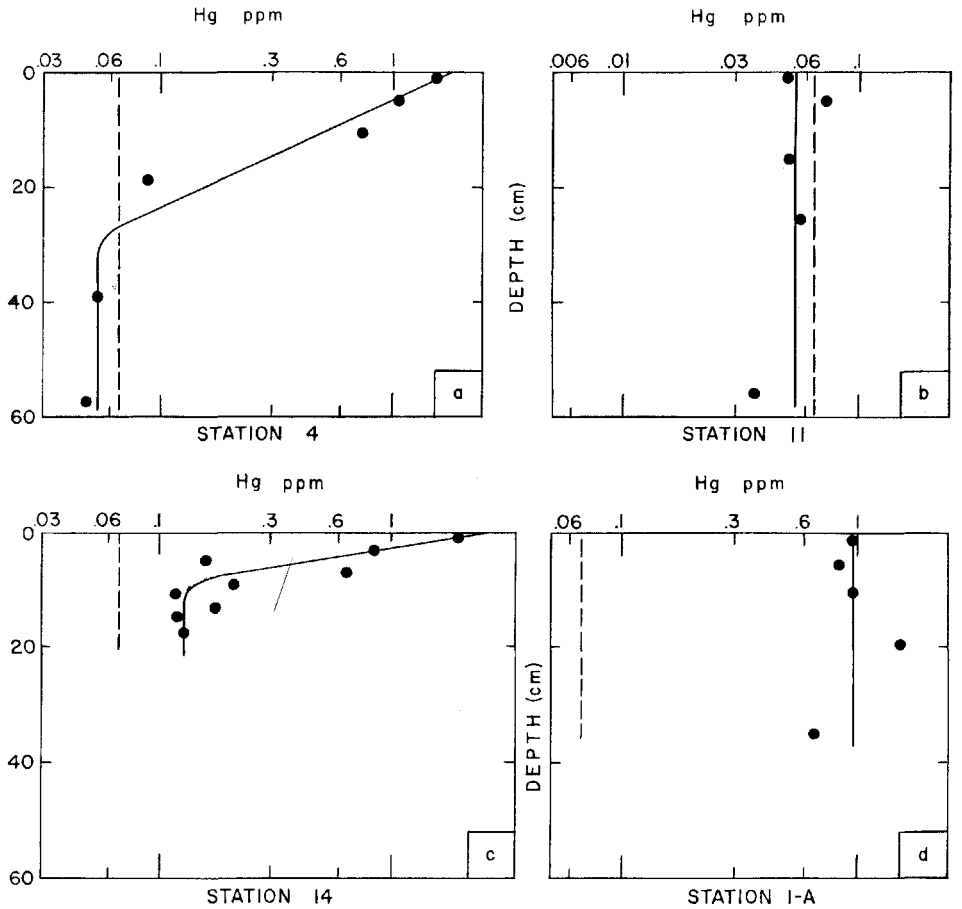

FIGURE 4. Patterns of mercury concentration as a function of depth for Lake Erie cores: (a) mercury-enriched surface zone overlying zone having natural background mercury levels, (b) zone with natural background mercury level and no mercury-enriched surface zone, (c) mercury-enriched surface zone overlying homogenized zone with abnormally high mercury levels, and (d) homogeneous zone with abnormally high mercury levels extending to the surface.

Mercury concentration in excess of the background level is due to pollution input into western Lake Erie. To be conservative, the critical level of 0.0675 ppm mercury dry basis was accepted as a background level for calculating the total mercury-pollution load.

Starting with the mercury-depth models given by Equation 1 and table 2, the pollution component is calculated as follows. First, because the values for mercury concentration in tables 1 and 2 are given in terms of dry sediment, they must be corrected for the water content of the sediment. Thus the weight percent

water in the sediment, as given in table 1, was converted to porosity, according to the following equation of Berner (1971).

$$\phi = \frac{\rho_s}{\rho_s + (1-w)\rho_w} \qquad \text{(Equation 4)}$$

where ϕ = sediment porosity,
w = weight percent water (wet weight)/100,
ρ_s = average density of sediment particles; assumed to be 2.6, and
ρ_w = density of pore water (assumed to be 1.0).

Then a porosity-depth model was calculated, according to the equation,

$$\phi(D) = Ae^{-\lambda D} + C \qquad \text{(Equation 5)}$$

where $\phi(D)$ = the sediment porosity at depth D,
A = the surface intercept of a rapidly decreasing component,
λ = the exponential decay constant, and
C = a constant term which is 0.25 or greater.

This calculation was made using the least-squares program FRANTIC by Rogers (1962). Now that analytic functions of both mercury concentration (Equation 1) and porosity (Equation 5) with depth are available, the pollution component is given by the integration of these functions between the sediment-water interface and 20 cm, or some depth where the mercury model intersects the critical background level (0.0675 ppm mercury dry basis), as shown in the following equation.

Mercury pollution =

$$\int_0^{DMAX} [\rho_s Hg(D)(1-\phi(D)) - \rho_s 0.0675(1-\phi(D))]dD \qquad \text{(Equation 6)}$$

where DMAX = 20 cm or the depth at which Hg(D) by Equation 1 = 0.0675 ppm Hg,
ρ_s = the sediment density (assumed to be 2.6), and
D = depth below the sediment water interface.

Equations 1 and 5 are substituted into Equation 6, which is then integrated, and the result evaluated as a summation to give the mercury-pollution component in μgHg/cm^2.

$$\text{Pollution component} = 2.6 \sum_D \left[\left(\frac{A_1A_2}{(\lambda_1+\lambda_2)} e^{-(\lambda_1+\lambda_2)D} + \frac{A_2C_1}{\lambda_2} e^{-\lambda_2 D} + \frac{(C_2-1)}{\lambda_1} A_1 e^{-\lambda_1 D} + C_1 D - C_1C_2D \right) - 0.0675 \left(\frac{A_2}{\lambda_2} e^{-\lambda_2 D} + (1-C_2)D \right) \right]_D^{D+0.1} \qquad \text{(Equation 7)}$$

for $0 < D \leqslant 19.9$
and $Hg(D) > 0.0675$

where the subscript 1 refers to the parameters of the mercury-depth model (Equation 1), the subscript 2 refers to the porosity-depth model (Equation 5) given in table 2, and all parameters are defined as before.

The flow characteristics of the Detroit River water mass have been measured and identified by numerous authors (Hartley *et al.*, 1966; Herdendorf, 1969; Kovacik, 1972b; Walters *et al.*, 1972; and Walters and Herdendorf, 1973). Within the Detroit River, three water masses have been identified: a western-edge flow, a central flow, and an eastern-edge flow. These water masses maintain their continuity and can be traced into Lake Erie.

The distribution of mercury pollution shown in figure 5 is related to the flow characteristics of the Detroit River water masses. The sediment along the west bank of the Detroit River, which is carried by the western-edge flow, is highly polluted, containing up to 60 ppm mercury dry basis, downstream from the mouth of the Rouge River (Federal Water Quality Administration, 1970). Upstream from the Rouge River mouth, the mercury concentration in the Detroit River sediment was only 1 ppm. Over a long period of time, these polluted sediments

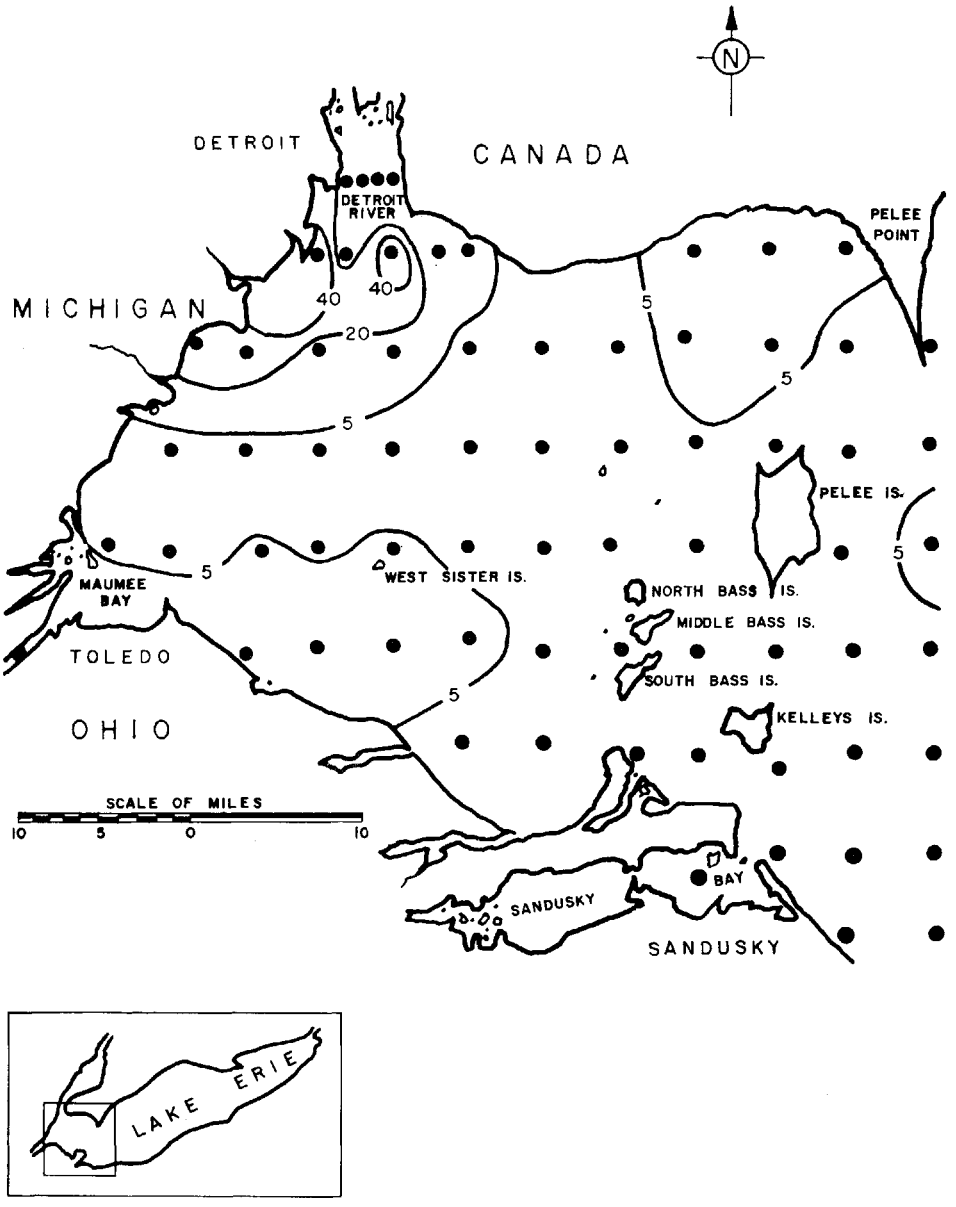

FIGURE 5. Mercury pollution in upper 20 cm of sediment in western Lake Erie. Units of mercury pollution are $\mu gHg/cm^2$.

are held near the western shore of Lake Erie (Kovacik and Walters, 1973) by average bottom currents that flow in a west-to-southwest direction (Federal Water Pollution Control Administration, 1968; Herdendorf, 1969); the currents are produced in part by the return flow of water from wind-driven surface currents in the opposite direction (Gedney and Lick, 1972). Deposition results in high-level mercury pollution south of the mouth of the Detroit River (fig. 5).

The mercury concentration north of Pelee Island (fig. 5) may be due partially to the eastern-edge flow of the Detroit River. Eastward-moving longshore currents along the Canadian shore may interact with north-moving longshore currents along the west wide of Pelee Point (Coakley, 1972, and Coakley and Cho, 1972) to produce a south-flowing bottom current at the location of the high mercury in the sediment. The dominant summer bottom flow around Pelee Island was observed to be counterclockwise (Federal Water Pollution Control Administration, 1968). The bottom currents developed in Pigeon Bay would tend to carry the mercury-laden sediment from the eastern-edge flow south from the Canadian shore toward Pelee Island.

A small contribution of mercury to western Lake Erie was demonstrated by core M–1 (table 1) from the Maumee River. The average mercury level measured for this core was 0.69 ppm. The results for two additional cores (not part of this study), which had average mercury concentrations of 0.14 and 0.19 ppm mercury dry basis, support the conclusion that Maumee River sediments are moderately polluted. If we assume, for purposes of discussion, that core M–1 is representative of the 2×10^6 metric tons/year sediment input from the Maumee River basin (Campbell *et al.*, 1969) in western Lake Erie, then the Maumee River has contributed a total of 39 metric tons of pollution mercury during the last 32 years. This amount of mercury is similar to that found in sediments along the south shore of western Lake Erie (fig. 5).

The total mercury-pollution load for western Lake Erie can be calculated from the data in figure 5 by multiplying the mercury-pollution component in $\mu gHg/cm^2$ times the surface area represented by each station. Summing these products gives 228 metric tons as the mercury-pollution load in Lake Erie sediments west of longitude 82°30′ west. This compares with 104 metric tons calculated for the amount of mercury released by the BASF Wyandotte Chemical Corporation, assuming the 9.1 kg/day estimate of the Federal Water Quality Administration (1970) for the period 1939 to 1970.

Additional mercury has been contributed to western Lake Erie by sediment carried by the Detroit River from Lake St. Clair, where sediments have been polluted by the effluent from the Dow Chemical plant at Sarnia, Ontario (Federal Water Quality Administration, 1970). Detroit River sediments upstream from the Rouge River mouth contain an average of 1.0 ppm mercury dry basis (Federal Water Quality Administration, 1970). Assuming that 15 years elapsed before appreciably polluted sediments were entering the Detroit River from Lake St. Clair (due to the time required for the sediment to cross Lake St. Clair), then the Dow Chemical plant at Sarnia, Ontario, has served as an effective mercury source to Lake Erie for the past 15 years. The 1.6×10^6 metric tons of sediment/year (Campbell, 1969) coming into Lake Erie from the Detroit River would have included a total of 16 metric tons of mercury that originated at the Sarnia, Ontario, plant. Based on these assumptions and calculations, a total of 69 percent of the estimated 228 metric tons of mercury pollution is accounted for by the combined input from the BASF Wyandotte Corporation, the Lake St. Clair-Detroit River system, and the Maumee River.

Two other sources of mercury input have not been included in this accounting. Agricultural use of organic-mercurial fungicides was prevalent prior to the time of initial pollution awareness in 1970. Prior to 1970, small amounts of organic mercurials were used as fungicides for agricultural seed grains. The contribution

from this source has not been estimated, but represents a basis for further research. This mercury could eventually have found its way into the Maumee River, and into other rivers draining northwestern Ohio and southeastern Michigan.

In addition, the burning of coal releases mercury, estimated at 3,000 metric tons of mercury/year (Joensuu, 1971), based on the conservative estimate of 1 ppm mercury in the world production of coal. Average analyses of coals vary considerably; Joensuu (1971) found an average of 3.3 ppm mercury in 25 coal samples from the United States, Ruch *et al.* (1971) found an average of 0.18 ppm mercury for Illinois coals, and Bertine and Goldberg (1971) estimated 0.012 ppm mercury for the average coal. Billings and Matson (1972) found that 90 percent of the mercury in coal is released to the environment in the flue gas of a large coal furnace. In this case, 2.5 kg/day was released by burning 7,750 metric tons of coal. The large metropolitan centers of Detroit-Windsor, Toledo, and Monroe have been significant coal users for many years, thereby contributing mercury to western Lake Erie either directly by atmospheric fallout or indirectly by surface-runoff transport of the fallout over the nearby land area.

Not considered in this mass balance is the mercury that escaped from the sediment, by whatever means. A major portion of this mercury enters the biological cycle and is concentrated by the food chain. This concentration process represents the basis for public concern (Seagram, 1970) mentioned earlier. Addition of the mercury contained in the biomass would raise the total pollution loading that was calculated.

CONCLUSIONS

The pollution input of mercury to western Lake Erie has been defined (Equation 7) as the mercury component in the sediment above a critical background level of 0.0675 ppm ($10^{-1.32+0.1}$) dry basis. Based on mathematical models for both mercury concentration and sediment porosity, the total load of mercury pollution in western Lake Erie sediments has been estimated to be 228 metric tons in the top 20 cm of sediment. This estimate is of the same order of magnitude as the total mercury input to the western basin from the combined reported contributions of Dow Chemical Corporation at Sarnia, BASF Wyandotte Chemical Corporation, Detroit River sediment, Maumee River sediment, and the burning of coal.

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REFERENCES CITED

Anikouchine, W. A. 1967. Dissolved chemical substances in compacting marine sediment. J. Geophys. Res. 72: 505–509.

Berner, R. A. 1971. Principles of chemical sedimentology. McGraw-Hill, New York. 240 p.

Bertine, K. K., and **E. D. Goldberg.** 1971. Fossil fuel combustion and the major sedimentary cycle. Science 173: 233–235.

Billings, C. E., and **W. R. Matson.** 1972. Mercury emissions from coal combustion. Science 176: 1232–1233.

Cameron, E. M., and **I. R. Jonasson.** 1972. Mercury in Precambrian shales of the Canadian Shield. Geochim. Cosmochim. Acta. 36: 985–1005.

Campbell, N. J., J. P. Bruce, J. F. Hendrickson, P. M. Higgins, C. Pemberton, Jr., W. A. Steggles, and **J. R. Valentyne,** eds. 1969. Pollution of Lake Erie, Lake Ontario, and the international section of the St. Lawrence River. Report to the International Joint Commission by the International Lake Erie Water Pollution Board and the International Lake Ontario-St. Lawrence River Water Pollution Board. Vol. 1. 151 p.

Coakley, J. P. 1972. Nearshore sediment studies in western Lake Erie. Proc. 15th Conf. Great Lakes Res., Internat. Assoc. Great Lakes Res.: 330–343.

Coakley, J. P., and **H. K. Cho.** 1972. Shore erosion in western Lake Erie. Proc. 15th Conf. Great Lakes Res., Internat. Assoc. Great Lakes Res.: 344–360.

Copeland, R. 1970. The mercury threat; questions to consider. Limnos. 3(2): 11–13.

Cranston, R. E., and **D. E. Buckley.** 1972. Mercury pathways in a river and estuary. Environ. Sci. Technol. 6: 274–278.

Federal Water Pollution Control Agency. 1968. Lake Erie Environmental Summary 1963-1964. U. S. Dept. Interior, Washington D.C. 1970 p.

Federal Water Quality Administration. 1970. Investigation of mercury in the St. Clair River-Lake Erie system. Open File Rept. 108 p.

Gedney, R. T., and **W. Lick.** 1972. Wind-driven currents in Lake Erie. J. Geophys. Res. 77: 2714–2723.

Hartley, R. P., C. E. Herdendorf, and **M. Keller.** 1966. Synoptic water sampling survey in the western basin of Lake Erie. Proc. 9th Conf. Great Lakes Res., University of Michigan Great Lakes Res. Div.: 301–322.

Hatch, W. R., and **W. L. Ott.** 1968. Determination of submicrogram quantities of mercury by atomic absorption spectrophotometry. Anal. Chem. 40: 2085–2087.

Herdendorf, C. E. 1969. Water masses and their movements in western Lake Erie. Ohio Dept. Natural Resources, Div. Geol. Survey Rept. Invest. No. 74. 7 p.

Joensuu, O. I. 1971. Fossil fuels as a source of mercury pollution. Science 172: 1027–1028.

Jones, T. A., and **W. R. James.** 1972. MAXLIKE: FORTRAN IV program for maximum likelihood estimation. Geocom Programs No. 5. 16 p.

Kalb, G. W. 1970. The determination of mercury in water and sediment samples by flameless atomic absorption. Atomic Absorption Newsletter 9(4): 84–87.

Kennedy, E. J., R. R. Ruch, and **N. F. Shimp.** 1971. Distribution of mercury in unconsolidated sediments from southern Lake Michigan. Ill. State Geol. Surv. Environ. Geol. Notes No. 44. 18 p.

Kovacik, T. L. 1972a. Distribution of mercury in western Lake Erie water and bottom sediments. Unpub. M.A. Thesis, Bowling Green State Univ., Bowling Green, Ohio. 74 p.

——— 1972b. Information on the velocity and flow pattern of Detroit River water in western Lake Erie revealed by an accidental salt spill. Ohio J. Sci. 72(2): 81–86.

Kovacik, T. L., and **L. J. Walters, Jr.** 1973. Mercury distribution in sediment cores from western Lake Erie. Proc. 16th Conf. on Great Lakes Res., Internat. Assoc. Great Lakes Res.: 252–259.

Manheim, F. T. 1970. The diffusion of ions in unconsolidated sediments. Earth Planet. Sci. Letter 9: 307–310.

Ontario Water Resources Commission. 1970. Report on the mercury pollution of the St. Clair River system. Open File Rept. 57 p.

Rogers, P. C. 1962. FRANTIC program for analysis of exponential growth and decay curves. Mass. Inst. of Technol. Lab. for Nuclear Sci. Tech. Rept. 76. 50 p.

Ruch, R. R., H. J. Gluskoter, and **E. J. Kennedy.** 1971. Mercury content of Illinois coals. Ill. State Geol. Survey Environ. Geol. Notes No. 43. 15 p.

Seagram, M. L. 1970. Mercury in Great Lakes fish. Limnos 3(2): 3–10.

Skoch, E. J., and **J. M. Turk.** 1972. Fluctuations in the level of mercury in sediments collected from the island area of Lake Erie, 1964 to 1968. Proc. 15th Conf. Great Lakes Res. Internat. Assoc. Great Lakes Res.: 291–297.

Syers, J. K., I. K. Iskandar, and **D. R. Keeney.** 1973. Distribution and background levels of mercury in sediment cores from selected Wisconsin lakes. Water, Air, and Soil Pollution 2: 105–118.

Tazur, A. 1971. Interstitial diffusion and advection of solute in accumulating sediments. J. Geophys. Res. 76: 4208–4211.

Thomas, R. L. 1972. The distribution of mercury in the sediments of Lake Ontario. Canad. J. Earth Science 9: 636–651.

Walters, L. J., Jr., C. E. Herdendorf, L. J. Charlesworth, Jr., H. K. Anders, W. B. Jackson, E. J. Skoch, D. K. Webb, T. L. Kovacik, and **C. S. Sikes.** 1972. Mercury contamination and its relation to other physico-chemical parameters in the western basin of Lake Erie. Proc. 15th Conf. Great Lakes Res., Internat. Assoc. Great Lakes Res.: 306–316.

Walters, L. J., Jr., and **C. E. Herdendorf.** 1973. Mercury concentration in surface sediments as related to water masses in western Lake Erie. Compass 50(4): 5–10.

Wood, J. M., F. S. Kennedy, and **C. G. Rosen.** 1968. Synthesis of methyl-mercury compounds by extracts of a methanogenic bacterium. Nature 220: 173–174.